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(54) THERMOSETTING RESIN COMPOSITION, ADHESIVE SHEET, AND ADHESIVE-BACKED METAL FOIL

(57) Abstract:

PURPOSE: To obtain a thermosetting resin composition which becomes flowable upon heating, is excellent in heat resistance and adhesion, and is usable for bonding at 180°C or below; and to obtain an adhesive sheet and an adhesive- backed metal foil which are applications of the composition as an adhesive.

CONSTITUTION: The composition comprises a linear epoxy polymer obtained by polymerizing a bifunctional epoxy resin with a bifunctional phenol in an equivalent ratio of the epoxy group to the phenolic hydroxyl group of 1/(0.9-1.1), a resin having dihydrobenzoxazine rings, and a polyfunctional epoxy resin.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention is excellent in the thermal resistance which can be used for a printed circuit board, TAB, a compound leadframe, the charge of plywood, etc., and relates to the thermosetting resin constituent which can carry out adhesion hardening at low temperature, the adhesives sheet using this, and metallic foil with adhesives.

[0002]

[Description of the Prior Art] The epoxy resin constituent which blended the macromolecule epoxy polymer, polyfunctional epoxy resin, and curing agent which have film organization potency as a resin constituent of an epoxy system among the insulating adhesives for electronic material is known (refer to JP,5-25368,A). Moreover, adhesion hardening can be carried out at low temperature, and what consists of a polyimide, polymaleimide, and an epoxy resin is known as a polyimide resin constituent with thermal resistance (refer to JP,5-339344,A).

[0003]

[Problem(s) to be Solved by the Invention] However, the resin constituent of this epoxy system has low thermal resistance, cannot maintain the elastic modulus in the elevated temperature of a resin constituent about the use in a COB (chip onboard) substrate and BGA (ball grid array) substrate isoelectronic part field, but has the fault that poor wirebonding at the time of chip mounting is not avoided. On the other hand, like the multilayering adhesion in multilayer-board manufacture, although it is useful to adhesion between flat surfaces in order not to carry out a melting flow, even if it heats a polyimide resin constituent, since it embeds the crevice between circuits, it is inapplicable to the use which needs the fluidity of adhesives.

[0004] this invention has a fluidity, when it heats, and it excels in thermal resistance and an adhesive property, and the metallic foil with an adhesives sheet and adhesives which is the thermosetting resin constituent which can be pasted up, and an application product as adhesives of this thermosetting resin constituent at low temperature 180 degrees C or less is offered.

[0005]

[Means for Solving the Problem] As a result of repeating research wholeheartedly, by blending with a straight chain-like epoxy polymer [****] the resin and polyfunctional epoxy resin which have a dihydrobenzo oxazine ring, this invention persons find out that the aforementioned technical problem is solved, and came to complete this invention based on this knowledge. That is, this invention offers the thermosetting resin constituent which blended the resin and polyfunctional epoxy resin which have a dihydrobenzo oxazine ring with the straight chain-like epoxy polymer which is made to carry out the polymerization of a 2 organic-functions epoxy resin and the 2 organic-functions phenols by epoxy-group / phenol hydroxyl-group =1/(0.9-1.1) equivalent ratio, and is obtained.

[0006] The straight chain-like epoxy polymer used by this invention is obtained by considering as epoxy-group / phenol hydroxyl-group =1/(0.9-1.1), and the boiling point's being 5 - 50 % of the weight of reaction solid-content concentration among an amide system solvent 130 degrees C or more under existence of a catalyst, heating the combination equivalent ratio of a 2 organic-functions epoxy resin and 2 organic-functions phenols, and carrying out the polymerization of a 2 organic-functions epoxy resin and the 2 organic-functions phenols.

[0007] If a 2 organic-functions epoxy resin is a compound which has two epoxy groups in a molecule, what thing is sufficient as it, for example, it has the bisphenol A type epoxy resin, a bisphenol female mold epoxy resin, a bisphenol S type epoxy resin, a cycloaliphatic epoxy resin, an aliphatic chain-like epoxy resin, the diglycidyl ether ghost of 2 organic-functions phenols, the diglycidyl ether ghosts of 2

organic-functions alcohols, these halogenides, these hydrogenation objects, etc. There is no limit in the molecular weight of these compounds. Moreover, several kinds of these compounds can be used together. Components other than a 2 organic-functions epoxy resin may be contained as an impurity. [0008] 2 organic-functions phenols have bisphenol A which is the hydroquinone which what thing is sufficient as as long as it is a compound with two phenolic hydroxyl groups, for example, is a monocyte 2 organic-functions phenol, a resorcinol, a catechol, and a polycyclic 2 organic-functions phenol, Bisphenols F and these halogenides, an alkylation object, etc. There is no limit also in the molecular weight of these compounds. Several kinds can be used together for these compounds like a 2 organic-functions epoxy resin. Moreover, components other than a 2 organic-functions phenol may be contained as an impurity.

[0009] If the catalyst for carrying out the polymerization of a 2 organic-functions epoxy resin and the 2 organic-functions phenols is a compound with the catalyst function in which the etherification reaction of an epoxy group and a phenolic hydroxyl group is promoted, what thing may be used, for example, an alkali metal compound, an alkaline-earth-metal compound, imidazole derivatives, an organic phosphorus compound, a secondary amine, a tertiary amine, quarternary ammonium salt, etc. will be mentioned. As an example of an alkali metal compound, the hydroxide of sodium, a lithium, or a potassium, a halogenide, organic acid chloride, an alcoholate, a phenolate, a hydride, a HOU hydride, an amide, etc. are mentioned. These catalysts can be used together.

[0010] An amide system solvent has a formamide, N-methyl formamide, N,N-dimethylformamide, acetamide, N-methyl acetamide, N, and N-dimethylacetamide, N and N, N', and N'-tetramethylurea, 2-pyrrolidone, N-methyl pyrrolidone, carbamic-acid ester, etc. that what is necessary is just what dissolves the 2 organic-functions epoxy resin used as a raw material, and 2 organic-functions phenols. These solvents can be used together. Moreover, you may use together with the solvent of others which are represented by a ketone system solvent and the ether system solvent.

[0011] The combination equivalent ratio of a 2 organic-functions epoxy resin and 2 organic-functions phenols may be epoxy-group / phenolic hydroxyl group =1/(0.9-1.1). If the equivalent of a phenolic hydroxyl group is smaller than 0.9Eq, it does not macromolecule-ize in the shape of a straight chain, but side reaction will occur and construct a bridge and a resin will become insoluble at a solvent. If the equivalent of a phenolic hydroxyl group is larger than 1.1Eq, macromolecule-ization of a resin will not progress.

[0012] Although especially the loadings of a catalyst are not restricted, generally a catalyst is about 0.0001-0.2 mols to one mol of 2 organic-functions epoxy resins. If [than 0.2 mols] more [a macromolecule quantification reaction is remarkably slow when there are few loadings of a catalyst to one mol of 2 organic-functions epoxy resins than 0.0001 mols, and], side reaction increases and macromolecule quantification may not be carried out at the shape of a straight chain.

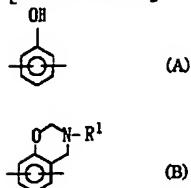
[0013] Although the solid-content concentration in the case of the polymerization reaction using the amide system solvent should just be below 50% (it is below the same% of the weight), it is preferably [10 - 30% of] good. Side reaction increases as it becomes high concentration, and it is hard coming to carry out macromolecule quantification at the shape of a straight chain. In low concentration, it is more difficult than 10% for a reaction to carry out macromolecule quantification late. Therefore, what is necessary is to make reaction temperature low and just to lessen the amount of catalysts, when polymerization reaction tends to be comparatively performed by high concentration and it is moreover going to obtain the straight chain-like amount epoxy polymer of macromolecules. If the molecular weight of the amount epoxy polymer of macromolecules is molecular weight from which there is film organization potency by the resin independent, and sheet-like adhesives are obtained, it is satisfactory. Such molecular weight is 70,000 or more in general. Furthermore, it is 100,000-150,000 preferably. In addition, especially the upper limit of the molecular weight of the epoxy polymer of the amount of macromolecules is not limited. However, in practice, or more by 150,000, since measurement of exact molecular weight is difficult and serves as hyperviscosity, the handling as a varnish becomes difficult.

[0014] 70-110 degrees C, preferably, it adds in the aldehyde which heated the mixture of the compound and the 1st class amine which have a phenolic hydroxyl group at 70 degrees C or more, and the resin which has the dihydrobenzo oxazine ring blended with the amount epoxy polymer of macromolecules is made to react at 90-100 degrees C for 20 to 120 minutes, and at the temperature of 120 degrees C or less, reduced pressure drying of it is carried out, and it is obtained after that.

[0015] The compound which has a phenolic hydroxyl group can mention phenol resin, such as a phenol novolak resin, a resol resin, a phenol conversion xylene resin, an alkylphenol resin, a

melamine phenolic resin, and polybutadiene denaturation phenol resin, a bisphenol compound, a biphenol compound, a tris phenolic compound, and a tetrapod phenolic compound. Moreover, it has the structural unit B to which the resin which has a dihydrobenzo oxazine ring when using phenol resin is expressed with the structural unit A expressed with the following formula (A), and the following formula (B), and when the mole ratio (A/B) of a structural unit A and a structural unit B is 1/(0.25-29) and it is the resin which each structural unit has combined through a direct or organic basis, intensity and the hardened material which was excellent in respect of thermal resistance can be obtained.

[Formula 2]



(However, R1 is a methyl group, a cyclohexyl machine, a phenyl group, or a substitution phenyl group, and the hydrogen of the ring of a structural unit A and a structural unit B may be replaced by arbitrary substituents except for one of the ortho positions of the hydroxyl of a structural unit A.) [0016] As the 1st class amine, substitution anilines, such as a monomethylamine, a cyclohexylamine, an aniline, a toluidine, and a xylylidine, etc. are mentioned concretely. Although hardening of the obtained resin is quick when a fatty amine is used, the thermal resistance of a hardened material is a little inferior. Hardenability becomes late although the thermal resistance of a hardened material is good when an aromatic amine like an aniline is used.

[0017] Moreover, as a polyfunctional epoxy resin blended with the amount epoxy polymer of macromolecules, the following epoxy compounds which have an average of two or more epoxy groups per molecule are mentioned. A bisphenol system epoxy resin, a halogenation bisphenol system epoxy resin, a bisphenol novolak system epoxy resin, a halogenation bisphenol novolak system epoxy resin, a phenol novolak system epoxy resin, a halogenation phenol novolak system epoxy resin, an alkylphenol novolak system epoxy resin, a polyphenol system epoxy resin, a polyglycol system epoxy resin, an annular aliphatic system epoxy resin. these are independent -- or two or more sorts are mixed and it is used

[0018] As for the blending ratio of coal of the resin which has the amount epoxy polymer of macromolecules and dihydrobenzo oxazine ring in this invention, and a polyfunctional epoxy resin, it is desirable that the amount epoxy polymer of macromolecules consider as 40 - 70 % of the weight. If the amount epoxy polymer of macromolecules is less than 40 % of the weight, a resin constituent will become weak and handling will become difficulty. If % of the weight is exceeded 70%, like the multilayering adhesion in multilayer-board structure, in the use pasted up while burying irregularity, the fluidity of adhesives will run short and concavo-convex embedding will become inadequate. Furthermore, as for the resin and polyfunctional epoxy resin which have a dihydrobenzo oxazine ring, it is desirable that use together and each is blended 15% of the weight or more. Unless the resin containing a dihydrobenzo oxazine ring is blended, the glass transition temperature and softening temperature of a resin constituent after heat hardening fall, and the elastic modulus in an elevated temperature cannot be maintained. If a polyfunctional epoxy resin is not blended, it is because an adhesive property is inferior.

[0019] If the resin constituent of this invention is preferably fabricated 0.01-0.1mm in the shape of a sheet beforehand and is used as sheet-like adhesives, it is expedient. Moreover, the resin constituent of this invention is sunk into a glass fabric, a fiberglass mat, aromatic-polyamide fiber cloth, an aromatic-polyamide fiber mat, etc. as a varnish, semi-hardening of the resin can be carried out and it can also be used as fiber strengthening type sheet-like adhesives.

[0020] The resin constituent of this invention is used as a varnish, and it applies and dries in an adhesion object as it is, and heating pressurization may be carried out with other adhesion objects, and you may paste up. In this case, it is desirable to carry out heating pressurization 20 minutes or more by the temperature of 100-250 degrees C and pressure 0.1-10MPa. It is more desirable to carry out heating pressurization especially for 60 to 120 minutes by the temperature of 150-200 degrees C and pressure 1-4MPa.

[0021] The metallic foil with adhesives which used the resin constituent of this invention as the

varnish, applied this varnish to one side of metallic foil, and was dried is useful to especially manufacture of the multilayered circuit board which has IVH (Interstitial Via Hole).

[0022]

[Example]

1.77g of sodium hydroxides was dissolved [as an example 1 (composition of amount epoxy polymer of macromolecules) 2 organic-functions epoxy resin] in 547.9g of N.N-dimethylformamide which is an amide system solvent as 115.5g (hydroxyl equivalent : 115.5) of bisphenol A, and a etherification catalyst as 177.5g (weight per epoxy equivalent : 177.5) of the bisphenol A type epoxy resins, and 2 organic-functions phenols, and solid-content concentration in the system of reaction was made into 30 % of the weight. Stirring this mechanically, in the 125-degree C oil bath, the temperature in the system of reaction was kept at 120 degrees C, and was stirred as it was for 4 hours. Consequently, viscosity was saturated with 12,800 mPa·s and the reaction was completed. The weight average molecular weight of the obtained amount epoxy polymer of macromolecules was 59,200 in the result measured by 72,500 and the light scattering measurement in the result measured by the gel permeation chromatography. Moreover, the reduced viscosity of the dilute solution of this amount epoxy resin of macromolecules was 0.770 dl/g.

[0023] (Composition of a resin which has a dihydrobenzo oxazine ring) 170g (an equivalent for 1.6 mols of hydroxyls) of phenol novolak resins was mixed with aniline 93g (one mol), it stirred at 80 degrees C for 5 hours, and the uniform mixed solution was prepared. Formalin 162g was taught into the 1l. flask, it heated at 90 degrees C, and a novolak / aniline mixed liquor was added little by little over 30 minutes. It maintained at reflux temperature and the reaction was made to complete for 30 minutes after an addition end. Furthermore, it decompressed to 7 or less kPas at 100 degrees C for 2 hours, condensation water was removed, and 71% of the hydroxyl which can react obtained the thermosetting resin formed into dihydrobenzo oxazine.

[0024] 40g of resins and 40g (weight per epoxy equivalent 177.5) of the bisphenol A type epoxy resins which have a dihydrobenzo oxazine ring were dissolved in the 400g (30-% of the weight solution) of the obtained amount epoxy polymer solutions of macromolecules, and it considered as the varnish.

[0025] The obtained varnish was cast on the glass plate, and it tore off from the glass plate after dryness for 10 minutes at 100 degrees C, fixed to the iron frame, and dried for 15 minutes at 140 degrees C, and the sheet with a thickness of 50 micrometers was obtained.

[0026] The inner layer circuit was formed in both sides of a glass base-material epoxy double-sided copper-clad laminate (thickness of 0.2mm, 18 micrometers of copper foils), the copper foil with an adhesives sheet and a thickness of 35 micrometers obtained above by the both sides was allotted, heating pressurization was carried out for 90 minutes by 180 degrees C and 3MPa, and the four-layer shield board was obtained.

[0027] The varnish obtained in the example 2 example 1 was applied to the roughening side of a copper foil with a thickness of 35 micrometers, it heated for 15 minutes at 140 degrees C continuously for 10 minutes by 100 degrees C, the adhesives layer with a thickness of 50 micrometers was prepared, and the adhesives sheet with a copper foil was obtained. The obtained adhesives sheet with a copper foil was used instead of the adhesives sheet of an example 1, and the copper foil, and the four-layer shield board was produced by carrying out heating pressurization on an example 1 and these conditions.

[0028] 400g [of the amount epoxy polymer solutions of macromolecules obtained in the example of comparison 1 example 1] (30-% of the weight solution), 80g [of the bisphenol A type epoxy resins] (weight per epoxy equivalent 177.5), and dicyandiamide 4.73g, 2-ethyl-4-methyl imidazole 0.45g, and 10g of N.N-dimethylformamide were stirred, it considered as the varnish, and the adhesives sheet was obtained like the example. The four-layer shield board was obtained like the example 1 using the obtained adhesives sheet.

[0029] The adhesives sheet with a copper foil was obtained on an example 2 and these conditions using the varnish obtained in the example 1 of example of comparison 2 comparison. The four-layer shield board was obtained by carrying out heating pressurization on an example 2 and these conditions using the obtained adhesives sheet with a copper foil.

[0030] The four-layer shield board was obtained by carrying out heating pressurization on the same composition as an example 1, and these conditions using the adhesives sheet of the polyimide system of example of comparison 3 marketing.

[0031] Change of the appearance after *****ing and floating an outer layer copper foil on the

resin restoration nature to a inner layer circuit, an outer layer copper-foil peel strength (kN/m), and a 288-degree C solder bath for 30 seconds about the four-layer shield board obtained in the above each example and example of comparison was investigated.

[0032]

[Table 1]

	実施例1	実施例2	比較例1	比較例2	比較例3
充填性	良好	良好	ポイド発生	ポイド発生	ポイド発生
ピール強度	2.04	1.87	2.12	1.98	1.57
はんだ耐熱性	良好	良好	ふくれ発生	ふくれ発生	ふくれ発生

[0033]

[Effect of the Invention] It can excel in thermal resistance and an adhesive property, and can paste up at low temperature, and the thermosetting resin constituent of this invention can be beforehand processed in the shape of a sheet. Furthermore, since it is meltable to a solvent, it can apply to an adhesion object beforehand and can also be made to paste up with other adhesion objects. Unlike the conventional sheet-like adhesives, since there is a fluidity of adhesives, the sheet-like adhesives of this invention can be used suitable for adhesion of the inner layer circuit of a multilayer printed wiring board. Moreover, since IVH is producible simple by carrying out multilayering adhesion beforehand after making a hole with a drill etc., the metallic foil with adhesives of this invention is used suitable for manufacture of the multilayered circuit board which has IVH.

[Translation done.]